Appendix C

to

ELECTRON MICROPROBE/SIMS ANALYSES OF Al IN OLIVINE: APPLICATIONS TO SOLAR WIND, PALLASITES, AND TRACE ELEMENT ANALYSES.

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SIMS Analyses of San Carlos olivine

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Analytical Conditions

Caltech Cameca 7f Geo

Table S1

nA(1)	Impact E (keV)	Sample HV (kV)	spot (2) (µm)	Raster (µm)	Egate(3) %	FA (4) (µm)	MRP (5)
20	22	8.8	25	75	80	200	3000

(1) O^- primary ion beam current. Constant to around 1%
(2) Primary ion beam spot diameter.
(3) Electronic gating; percentage of raster dimension.
(4) Field aperture. Actual diameter. Focused to approximately 12 µm on sample.
(5) Mass Resolving Power (exit slits)

In addition to measuring Al with the electron multiplier (EM) detector, as possible matrix ions ^{24}Mg (Faraday cup), ^{30}Si, and ^{56}Fe (both on EM) were analyzed. The relatively high mass resolving power was required to resolve ^{27}Al from ^{26}MgH, Si_2 from ^{56}Fe and ^{30}Si from ^{29}SiH. Mass scans demonstrated adequate peak resolution.

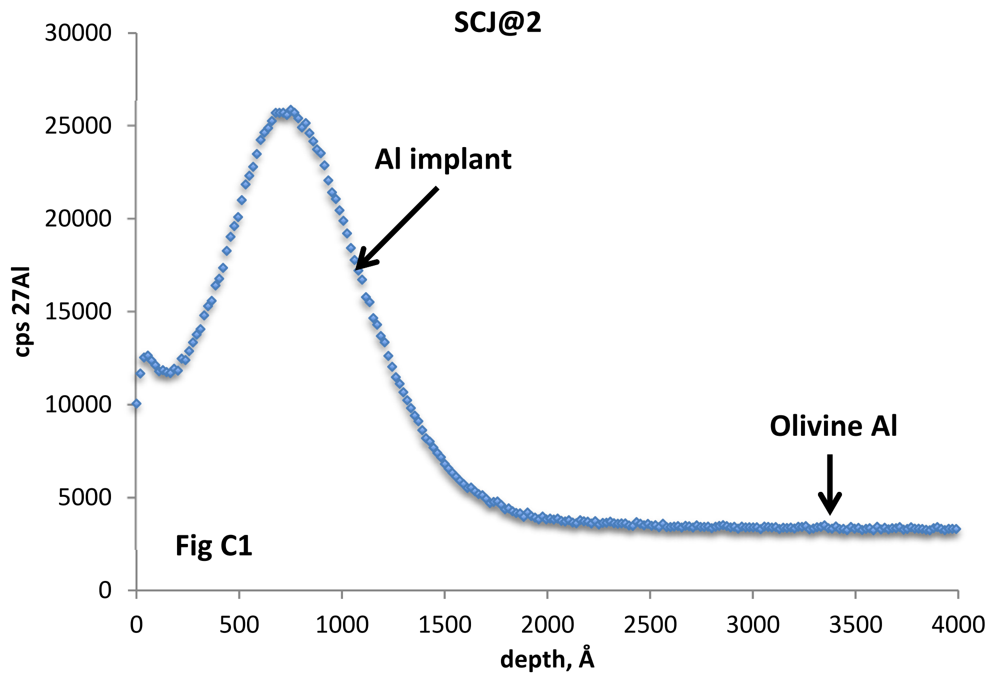


Fig C1

Figure C1 (same as text figure 1) shows a typical SCJ implant depth profile for 80 keV Al.

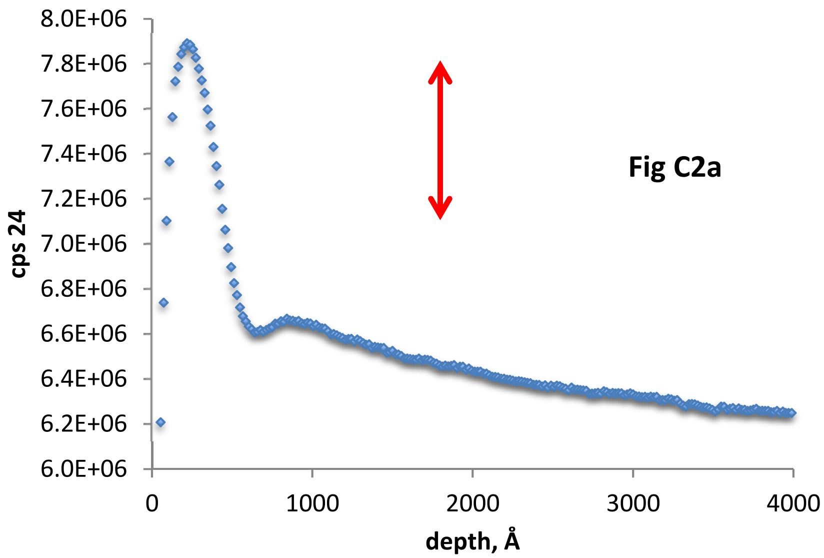
The Al added by the 5e14/cm^2 fluence is equivalent to about 15-20 ppm in an electron probe analysis, which is not negligible. So, post-implant electron probe analysis of SCJ cannot be easily used to calibrate the implant.

Another issue with SCJ is the presence of Al-rich inclusions. These are seen in the deep olivine Al part of the profile beyond 300Å in 2/5 profiles.

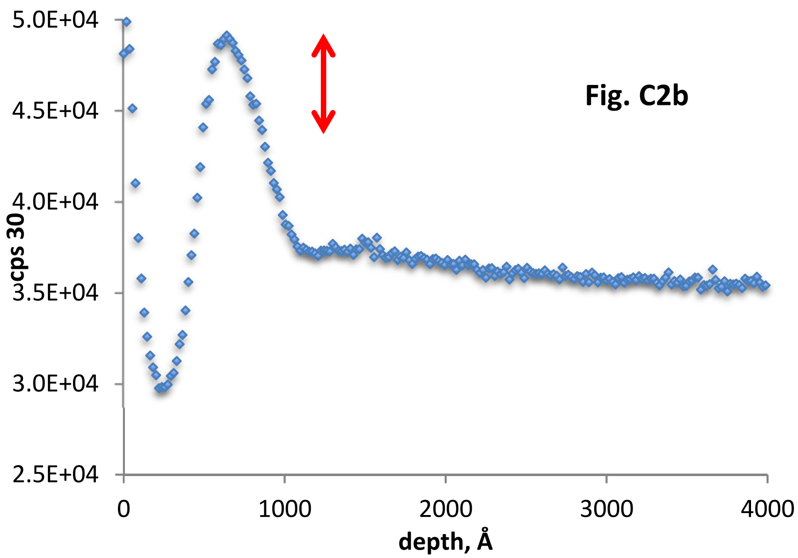
The larger of the two observed inclusions adds about 200 Al cps and would be difficult to see if present at implant depths shallower than 2000Å. However the inclusion is relatively thick, 1000-2000Å and if present anywhere within the implant profile would contribute 1.5-2% to the depth integral. To the extent that this is an upper limit, inclusions are an unimportant source of error in these data. Close inspection of the 3 depth profiles used showed very smooth profiles with no evidence for large inclusions.

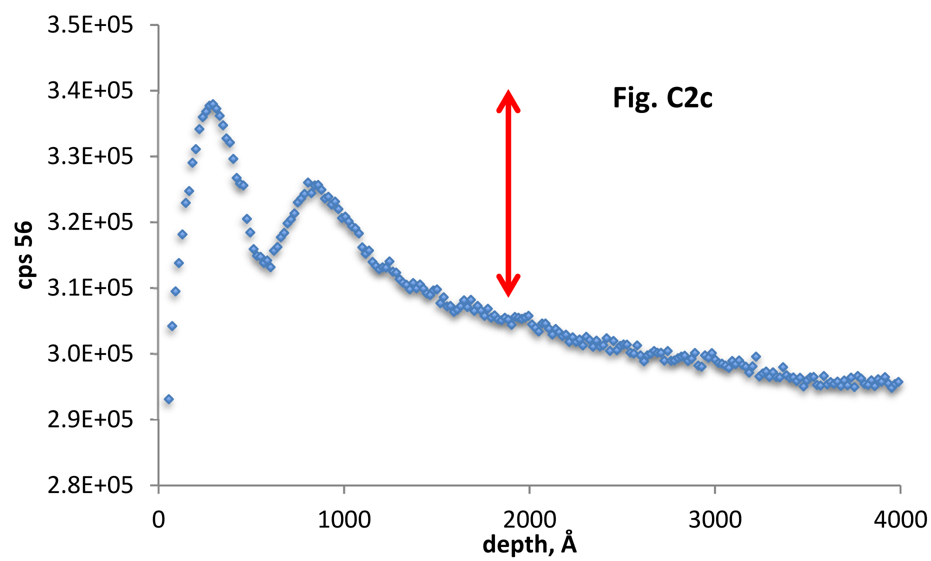
All depths scales in this paper refer to depths from the olivine surface, corrected for the effect of the conducting C coat based on the step in cps Al. Depth errors from this correction are not important.

Sputtering pit depths were measured by profilometry at Dartmouth. Replicate measurements (6-8) were made on each pit in 3 different sessions. The pit depths reproduced to 0.81 to 1.14%. Here we are calculating a fluence relative to a known olivine concentration; this requires knowing the absolute pit depth rather than the relative pit depths among different profiles. The profiliometer was calibrated relative to a NIST step standard, accurate to 1.3%. A correction of 3.8 ± 0.8% was applied to the measured pit depths. The total error in the pit depths and propagated into sputtering rates is 1.8%. In assessing fluence precision among different implant profiles, the relevant error from pit depth measurements is 1.3%.



Quantitative SIMS analysis requires steady state sputtering conditions. Figures C2abc show the large transient structure in the outer 1200-1500Å for matrix ^{24}Mg, ^{30}Si and ^{56}Fe depth profiles for the SCJ@2 analysis. Sputtering steady state is reached when the profiles show a smooth (due to charging) decline. The complex oscillating structure rules out quantitative SIMS analysis in the transient region using any of these ions for matrix normalization. For reference the peak depth of the Al implant profile (Figure C1) is 680Å, not deeper than the observed structures. Red arrows equal 10% variations in counting rate.





Transient effects, continued

The transient structure shown in Figures C2abc differs for the different matrix ions. Note the expanded y axis scales. The magnitudes of the various oscillations differ slightly; the red arrows give an approximate 10% variation. Two other SCJ matrix profiles show only minor variations from those shown in Figure C2 for profile SCJ@2, as do two matrix profiles from the unimplanted SC3 standard. SC3 allows evaluation of Al transients (Figure C3). The strong rise shallower than 500Å is a combination of transients and Al surface contamination. The small bump around 800Å is a transient feature; it is seen in the other SC3 profile. Also, 10-20 other SC3 Al profiles analyzed previously have shown no inclusions. The 800Å transient is worth at most 100 Al cps, but at 800Å for the SCJ implant (slightly deeper than the peak), this is less than 1 sigma counting statistics, so the 800Å Al transient bump has been ignored. The Al transient region is significantly smaller than that for Mg, Si, or Fe.

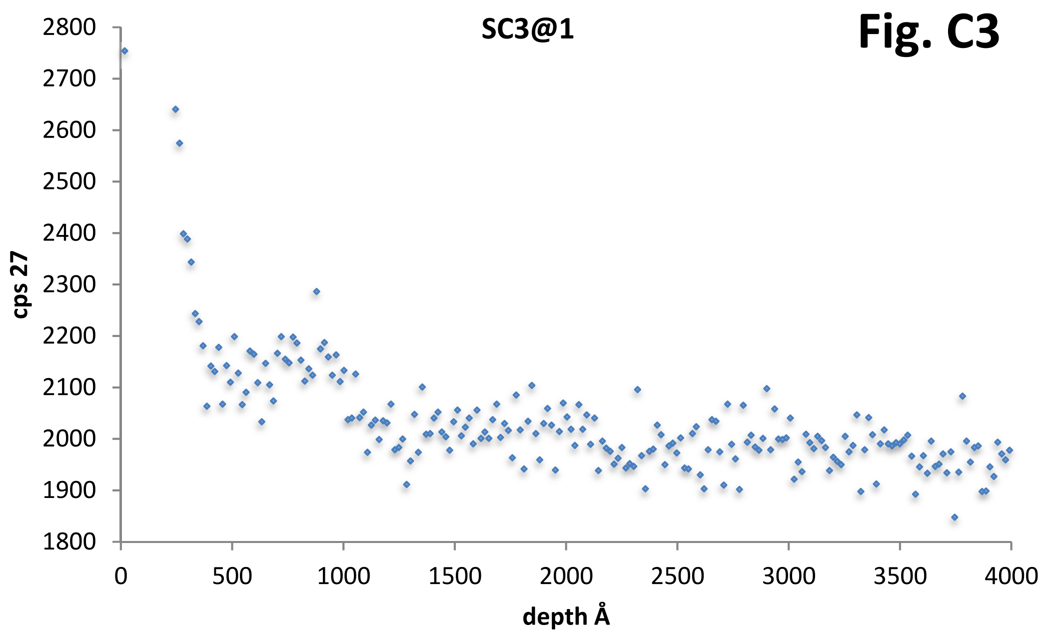


Fig. C3

Effect of oxygen flood on transients

In some cases the use of a low pressure of O_2 leaked into the sample chamber (O_2 flood) reduces transients. However, in this study, no improvement in the matrix ion transients were observed. SCJ profiles were made with and without the flood with all other conditions held constant. Chamber O_2 pressure was relatively constant at around 1.3×10^{-5} Torr. As expected the sputtering rate without the flood was higher by about a factor of 1.45, but when *depth* profiles were compared, only minor differences in matrix element transients were observed. All analyses reported were made without O_2 flood.

Choice of matrix ion

For our analyses, the primary ion beam current was constant to 1% or better. Why not just base quantitation on the measured cps Al? Why is it necessary to normalize the cps Al to some other ion counting rate? This is because there are other sources of counting rate drift, independent of beam current, and normalizing to some matrix ion counting rate tends to remove these. In our case, the charging counting rate decrease is of obvious importance.

For convenience, we repeat the equations for the calculation of the SCJ implant fluence from the text:

$$n(x) = RSF\ (Al/\ ^{24}Mg)_i\ (x) \quad (1)$$

$$\psi = \int n\ dx = RSF \int (Al/\ ^{24}Mg)_i\ dx \quad (2)$$

where n is the number of Al atoms/cc at depth x, ^{24}Mg is the matrix reference isotope, $(Al/\ ^{24}Mg)_i$ is the implant counting rate ratio, and ψ is the implant fluence in atoms/cm^2. The depth scale dx is related to the measured time step, dt and the sputtering rate S, where S is the pit depth (as discussed above) divided by the total sputtering time in olivine.

$$dx = S\ dt$$

Sputtering rates were 1.9 – 2.2 Å/sec

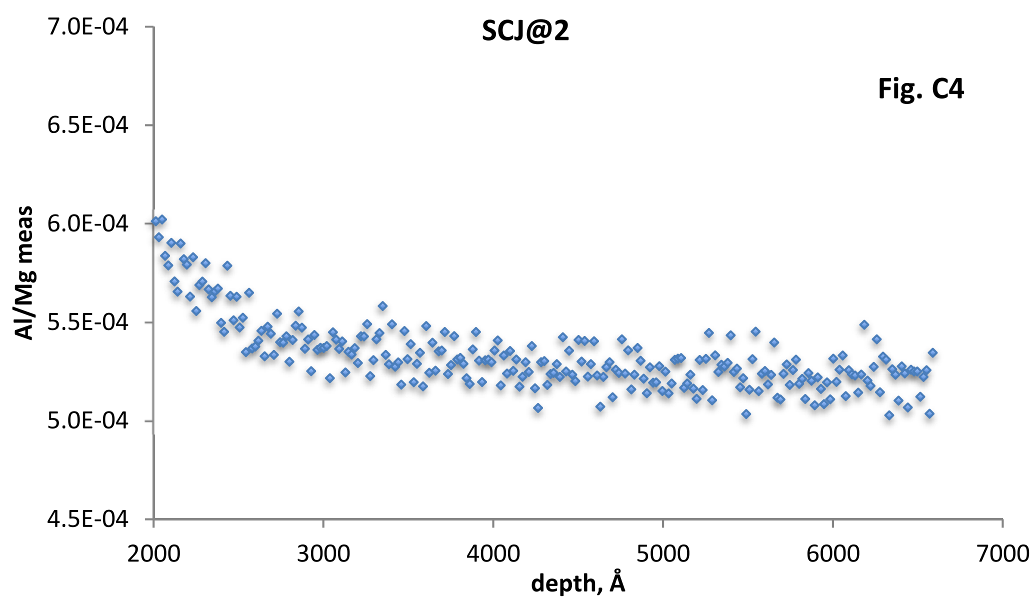
Ideally all of the implant should be measured in the steady state region, but comparison of Figures C1 and C2 shows that this is not possible in our case because of transient structure in all potential matrix ion profiles. Consequently, the depth integral (Eq 2) is divided into two parts: (1) a "main" integral using data from depths safely in the sputtering steady state regime; this requires a decision for as to where the lower limit of the main integral is safely within the steady state regime and (2) a "surface correction" for the portion of the implant profile in the transient region based on a theoretical implant depth profile.

Comparison of Figs C2 and C3 shows that all possible choices for the matrix ion have transient regions that extend deeper than the Al transient region, so that a choice for the main integral lower limit that avoids the matrix ion structure will be a safe choice for the Al profile.

Choice of matrix ion, continued

The Mg, Si, and Fe transient depth regions (Figure C2) extend to similar depths. The magnitude of the oscillations are greatest for Si and least for Fe. However, the Fe oscillations extend to deeper depths than Mg, so we have selected Mg as the matrix ion.

Even within the steady state region, counting rate profiles for all elements decrease due to charging, but the normalized Mg/Al profiles reach constant deep values (Fig. C4) for three (@2, @3, @4) of the four SCJ profiles measured, indicating the same charging variations for Mg and Al; the unimplanted SC3 profiles are very similar to these three. Despite constant beam current, profile SCJ@5 shows much larger decreases in the steady state region depth than the other profiles for unknown reasons (greater charging?); moreover the deep Mg/Al counting rate ratio does not reach a constant value at large depths, continuing to decrease throughout the measured profile, although the deepest Mg/Al ratio for SCJ@5 is close to the constant value for the other 3 profiles.



Choice of matrix ion, continued

Mg profile @2 (Figure C2a) shows a very small transient overshoot at 700-900Å, which cannot be seen in profiles @3 and @4. The overshoot in @2 is very small (order 0.1%) and has been ignored. In all profiles, the 600Å dip (Fig. C2a) is small, less than 2% relative to an extrapolation of the steady state trend in ^{24}Mg cps from deeper depths and could be ignored; however, as shown in Figure C5, a small correction is possible by extrapolating from the steady state charging trend at deeper depths.

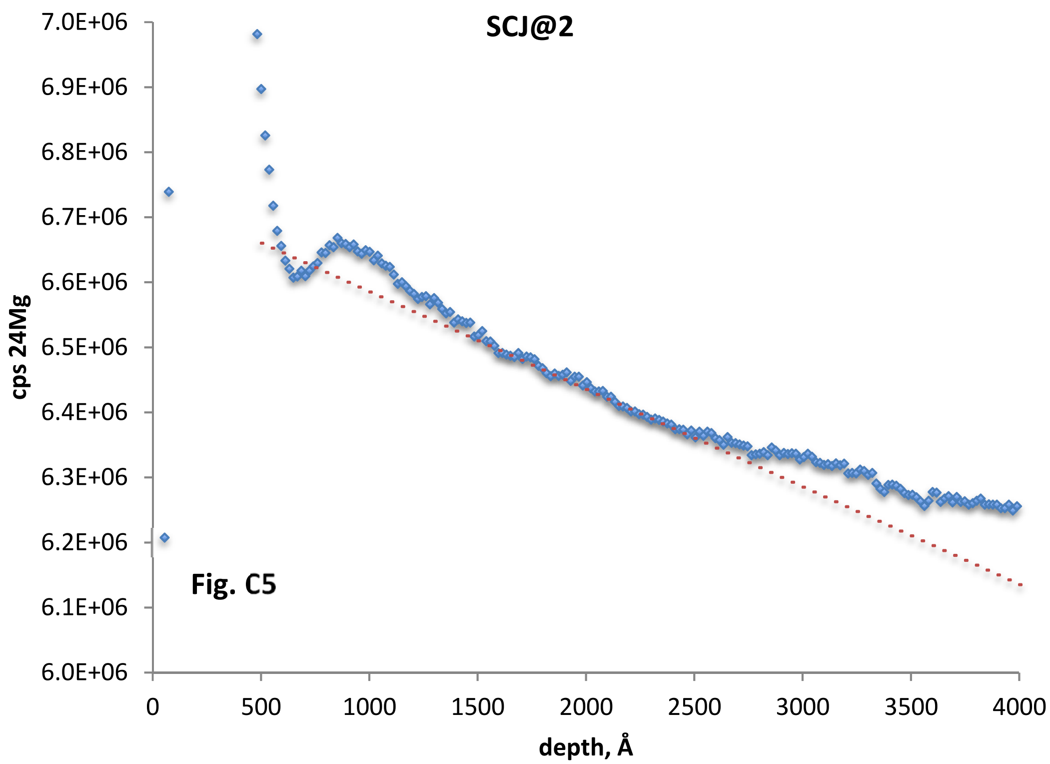


Fig. C5

Note the expanded y axis scale in Figure C5. Extrapolation of a linear fit to the ^{24}Mg counting rate, between 1450 to 2500Å (red line) to where it intersects the large 185Å transient peak at 612Å, provides an estimate of the ^{24}Mg counting rate unaffected by transients. Thus, for SCJ@2, the lower limit of the main depth integral is 612Å. The extrapolated red line was used as the the ^{24}Mg counting rate until 1633Å; beyond this, actual data were used.

Since the corrections are small, from 612Å to 1633Å, the measured Al/Mg was just scaled by the ratio of the measured to extrapolated ^{24}Mg counting rate. Similar 630Å dip corrections were applied to the @3 and @4 profiles. (The anomalous SCJ@5 profile did not show a 630Å dip) The corrections to the calculated fluence for the 630Å transient dip are all less than 1%.

Surface correction

Even after the 630Å dip correction to the ^{24}Mg counting rate described above, a significant part of the ($Al/^{24}Mg$) depth integral is still within the transient depth of the large 185Å peak in the ^{24}Mg counting rate. In the SCJ@2 example above, we need an estimate of the contribution of the depth integral below 612Å.

The surface correction was made by calculating the fluence below the main integral lower limit (612Å for SCJ@2) using a theoretical depth profile from the SRIM model (Ziegler et al., 2008).

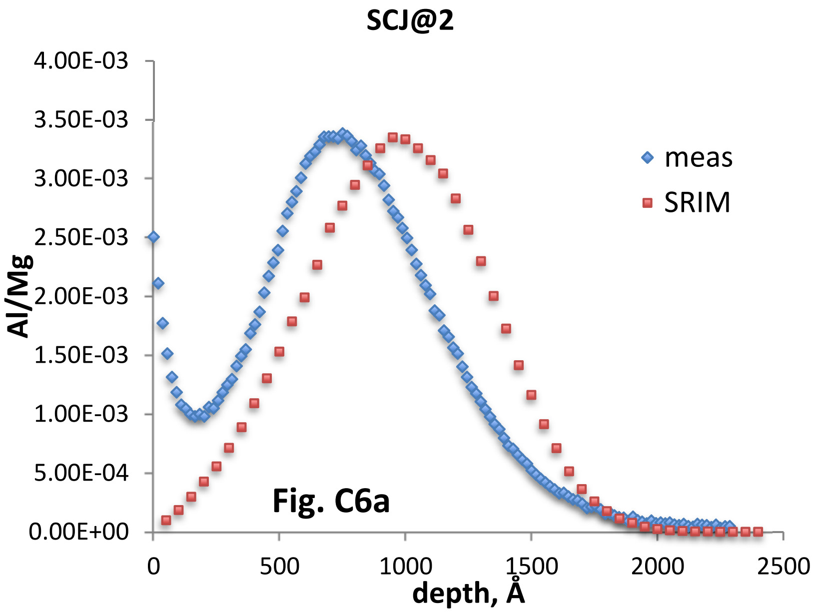


Fig. C6a

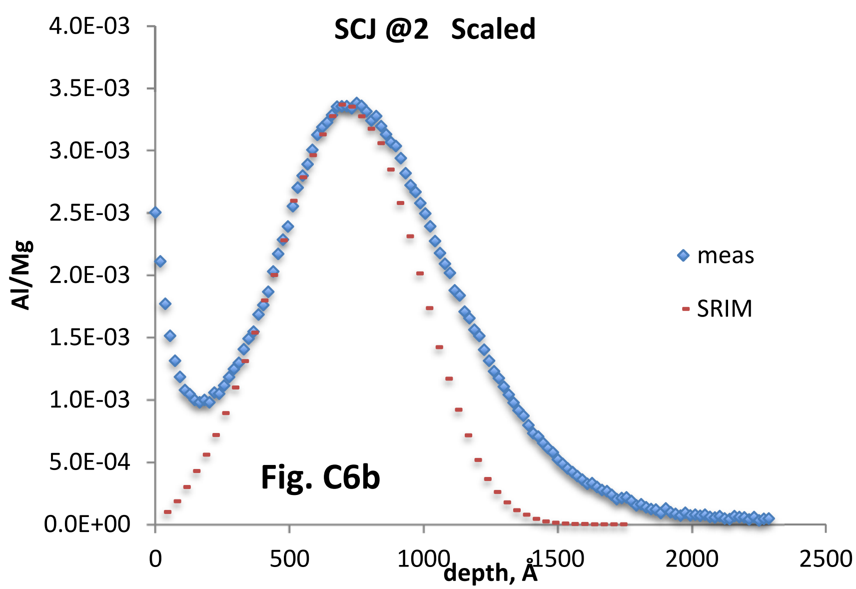


Fig. C6b

Figure C6a compares the measured and theoretical (SRIM) implant profile scaled to match the measured peak Al/Mg. The measured Al/Mg in Figures C6ab has been corrected for the olivine Al/Mg from the deeper part of the profile. The measured peak profile is shallower and broader on a proportional basis (Fig. C6b). The SCJ mount was C coated and grounded for the ion implantation, so reduction of the Al ion beam energy by charging during implantation is unlikely. Charging during SIMS analysis cannot be ruled out in this case; however, we observe similar differences with conducting samples.

<u>Surface correction, continued</u>

In order to obtain a fluence surface correction, the SRIM depth was scaled by a factor of 0.751 (Figure C6b). With this scaling, the measured SCJ@2 profile from 330Å to the peak around 700Å is well described, although the measured profile is observed to be significantly broader than SRIM. This is in part due to charging and part due to the gardening effect of the SIMS primary ion beam.

For SCJ@2, the main integral fluence starts from 612Å (Figure C5). The integral of the scaled SIM profile (Figure C6b) from the surface to 612Å is added to the main integral of the measured profile beyond 612Å to give a total depth integral which, accompanied by the RSF (next section), gives the SCJ implant fluence from equation (2)

Relative Sensitivity Factors

These are calculated from the SIMS (Al/^{24}Mg) counting rate ratio for the SC3 standard for which the olivine Al concentration was known from electron probe analysis (Eq. 1) with the electron probe n(Al) =5.19±0.07x10^{18} atoms/cc (see main text). With a uniform Al concentration, measurements can be made deeper than any transient effects; in practice, depths greater than 2000Å.

Two profiles gave good agreement:

	deep Mg/Al (10^{-4})	RSF (10^{22})
SC3@1	3.23	1.607
SC3@2	3.22	1.611

The two SC3 profiles were bracketed between 4 SCJ implant profiles. An RSF of 1.609±0.029 x 10^{22} was adopted. The (1 sigma) error in the electron probe measurement is 1.4% which includes an error in the Al concentration of the enstatite standard (see text). Calculation of n(Al) requires adopting a density (3.355) for which we assign an uncertainty of 1%. The precision of the SIMS analyses is estimated at 0.5%. Compounding all RSF errors gives 1.8% or 0.029 x 10^{22} (1 sigma).

SCJ implant fluence

The (Al/^{24}Mg) counting rate ratio for Eq. 2 is that of the implant. The measured (Al/^{24}Mg) profile is corrected for: (a) the SJC Al olivine background based on the deep part of the profile, (b) the 630Å dip in the Mg transient, as discussed above and (c) the surface fraction of the Al/Mg profile lost in the large 185Å Mg transient, as discussed above. Errors from counting statistics and the 630Å dip correction are negligible.

Even when the anomalous SCJ@5 profile is included, the standard deviation of the four olivine background (Al/^{24}Mg) measurements is only 0.6%. This shows that the SCJ olivine Al concentration is uniform, at least in the local area analyzed for this study. Dividing the background depth for SCJ@3, which is 4000Å long, into 3 different segments and comparing the effect on the calculation of the main fluence produced negligible differences of less than 0.1%.

Table C2

Profile	SCJ Fluence (10^{14} atoms/cm^2)	Surface corr., %	Main integral start (Å)	end	SCJ olivine ppm Al
SCJ@2	4.87±0.19	29	612	3581	112.3
SCJ@3	4.37±0.17	23	486	2378	113.7
SCJ@4	4.72±0.18	26	585	2482	112.2
SCJ@5	4.82±0.29	42	756	3603	113.0

Table C2 summarizes the results from the four non-flood SCJ implant profiles that bracket the SC3 standard analyses. The average peak of the implant is 728Å. The relatively high start depths (lower limit of the main integral) is a consequence of the large Mg matrix transient at 185Å, which in turn produces the large surface corrections. The widths of the implant Al/ ^{24}Mg profiles vary as shown by the range in end depths (main integral upper limit). These are determined visually by the depth at which the (Al/ ^{24}Mg) implant profile disappears under the olivine Al/^{24}Mg background (Figure C1). The derived fluences are quite insensitive to the choice of the main integral upper limit: if the much smaller end depth of SCJ@3 is used for SCJ@2, the main integral is only decreased by 0.7%. The differences in end depths reflect variable long tails in the depth profiles for unknown analytical reasons.

As discussed above, the SCJ@5 profile is anomalous in having (1) a much larger amount of charging, (2) the absence of a 630Å dip in the Mg profile, and (3) the failure of the (Al/ ^{24}Mg) to reach a constant value in the deeper regions of the profile. Using the ratio of ^{24}Mg cps at 1500Å to 3500Å as a measure of charging, this ratio has a value of 1.22 for SCJ@5 but 1.01 to 1.04 for the other three profiles. There is also a broadening of the 185Å Mg transient peak, perhaps related to charging, that swamps the 630Å dip and produces the high main integral start depth for SCJ@5.

Table C2, continued

The primary ion current was constant throughout these analyses, thus the goal in normalizing the Al counting rate to Mg is to compensate for charging and any other sensitivity drifts. A check on the success of this approach is whether the (Al/ ^{24}Mg) ratio is constant at depths beyond the Al implant. Except for SCJ@5, this criterion is met. For SCJ@5, although not constant, the deepest (Al/ ^{24}Mg) agreed with that for the other 3 profiles. However, the failure to reach a constant value, indicates that, for unknown reasons, sensitivity drifts were happening that were not the same for Al and Mg, which could result in fluence errors for SCJ@5.

Final SCJ Implant Fluence

Despite the anomalies in the SCJ@5 profile, which differs from the other 3 SCJ profile and, in terms of matrix ion profiles, from the unimplanted SC3 profiles, the SCJ@5 fluence is within the spread of the other 3 profiles. However, even if the SCJ@5 fluence is excluded, the average fluence is decreased by only 0.9%. The largest potential fluence error for a single profile is from the surface correction. A rough error estimate was made for profile SCJ@2 by calculating an alternative surface correction based on a linear extrapolation of the implant (Al/Mg) from the start of the main integral (604 Å for @2) to 0 at the surface. This gives a correction that is definitely too high, but it turns out higher only by 10%. Thus, for a surface correction of 30% the % error in the fluence is then small, order 3%. Interprofile fluence precision from uncertainties in sputtering rate are estimated at 1.3%. The error from the choice of the main integral lower limit is estimated at 1.9%. Other sources of error in the fluence precision are negligible.

The estimated precision for an individual profile is thus 3.9% (one sigma). The standard deviation of the three adopted profiles is higher (5.5 %) indicating some unrecognized systematic or underestimated error, most likely in the surface correction

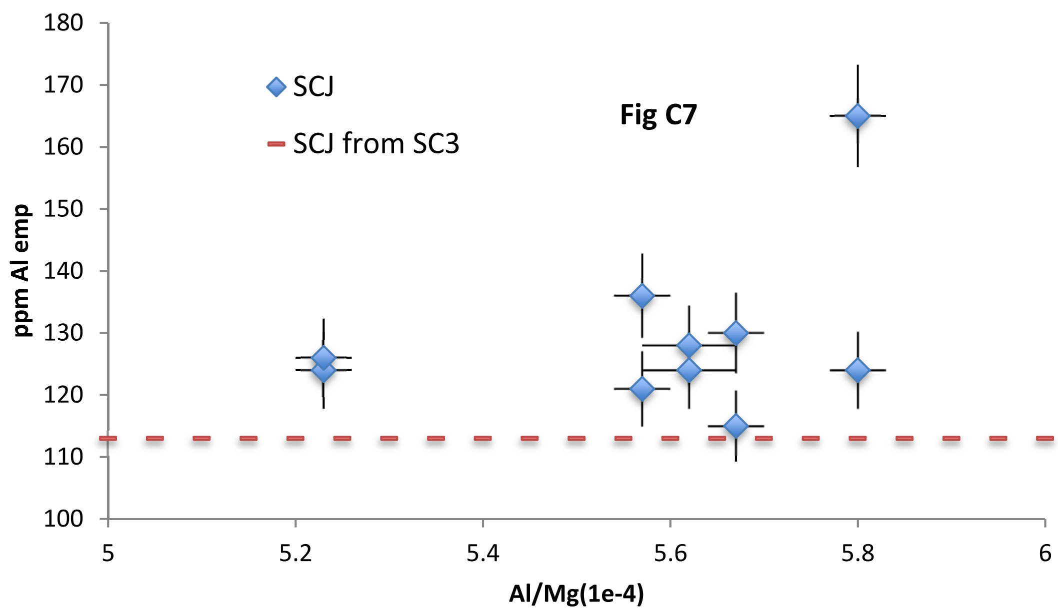
The measured 5.5% precision of the SCJ profiles is compounded with the 1.8% error in the RSF (slide 14) and the 1.3% error in the profilometer step standard to give a total error estimate of 6.0% or 0.28 x 10^{14} atoms/cm^2.

Adopted fluence of SCJ Al implant = 4.70±0.28 x 10^{14} atoms/cm^2

Quoted error is 1 sigma. As there may be unrecognized systematic errors, we do not adopt an error of the mean, although it would be justified statistically. The adopted fluence is in acceptable agreement with the nominal implant fluence of 5 x 10^{14} atoms/cm^2.

Al concentration of SCJ olivine

The relative sensitivity factor (RSF) derived from SIMS analysis of the SC3 EMP standard can be combined with the *olivine* (Al/ ^{24}Mg) of the SCJ profiles to measure the Al concentration of the SCJ olivine (Eq 1). All four SCJ profiles agree with 112-114 ppm Al (Table C2), based on the baseline (Al/ ^{24}Mg), excluding inclusions when present. Thus, ignoring some small Al-rich inclusions, the olivine in SCJ appears homogeneous in the few mm^2 area of the crystal where all analyses were made. The 113 ppm for SCJ is much higher than the 69 ppm for crystal SC3. Our survey electron probe measurements on San Carlos olivine crystals show significant (factor of about 2) variations among San Carlos olivine crystals.



The SCJ profiles calibrated relative to SC3 and reported above are from the 3rd in three SIMS sessions analyzing SCJ. Session 1 was prior to implantation. The selection of crystal SCJ for implantation was based on a SIMS survey of Al/^{24}Mg which indicated adequate homogeneity. We also made pre-implant electron probe (EMP) measurements of ppm Al with two EMP analyses made adjacent to each SIMS pit; the locations of the EMP analyses are thus accurately known. Fig. C7 compares the Al/Mg SIMS ratio (x-axis) with the EMP ppm Al for the session 1 comparison. There are two EMP measurements for each SIMS on Fig. C7. For clarity, Al/Mg for the cluster of 3 SIMS analyses around 5.6 has been displaced slightly on Fig. C7.

<u>Al concentration of SCJ, continued</u>

There are variations on Figure C7 but no correlation between the SIMS and EMP. The SIMS and EMP scales in Figure C7 are very different, with the EMP variations much larger. At the time of Session 1, we adopted a ±5% error to estimate homogeneity, but with hindsight, the precision of the SIMS Al/Mg is much higher. No inclusions were observed in the five Session 1 SIMS profiles, although it should be noted that much shorter profiles are needed in unimplanted samples. In all session 1 profiles the Al/Mg ratio was constant once transients died out. The SIMS counting statistics errors shown in Figure S7 are 0.4 to 0.8%. Three profiles agree at Al/Mg = 5.63×10^{-4} . Profile 5 is 2% higher and Profile 3 is 8% lower. Although relatively small, these variations appear real indicating Al inhomogeneity in SCJ at the 10% level. The counting statistics error bars on the EMP ppm Al are 5%. The total range in EMP analyses is 43%. If the anomalously high point at 165 ppm is rejected, the average Al is 125 ppm with a standard deviation of the data of 4.7%, in agreement with the 5% counting statistics standard deviation for a single analysis. The thicknesses of the Al-rich inclusions seen in the session 3 SIMS analyses are much less than 0.1 micron; even if these inclusions are lamellae with lateral dimensions large compared to the SIMS 50 micron spot size, they would contribute negligible Al to an EMP analysis. At the time of the session 1 EMP analyses, we were unaware of the complications discovered later and discussed in the manuscript text. The large 165 ppm analysis is best explained by Al contamination, which could also explain the difference between the 125 ppm Al from Session 1 EMP and the 113 ppm for the session 3 SCJ olivine concentrations based on the SIMS-cleaned electron probe data for SC3 (Table C2; dotted red line in Figure C7). Higher electron current densities were used in EMP analyses shown in Figure C7, so C deposition could also explain the 125 vs 113 ppm difference in Figure C7.

**Session 2 SIMS analyses of SCJ were post implant tests of SCJ implant quality in addition to pallasite analyses. In this case, an O_2 flood was used. Four SCJ profiles were run under the same conditions.
3 of 4 profiles showed small Al-rich inclusions. Two of the four profiles had baseline olivine Al/Mg ratios which agreed to within 0.2%. One measurement was 2% higher; another was 8% lower than baseline regions of olivine not affected by inclusions.**

Al concentration of SCJ, continued

Summarizing, Al-rich inclusions are found in 5/13 SCJ profiles, but these appear sufficiently small to not interfere with accurate EMP analyses of SCJ using the techniques described in the manuscript text for SC3. However, independent of inclusions, there appear to be up to 10% inhomogeneities in the Al concentration of SCJ.

The 6% accuracy in the SCJ implant fluence obtained in this study is acceptable, but could be improved somewhat if the RSF were calculated based on an accurately known EMP Al concentration for SCJ which would serve as an internal standard, as opposed to the external standard approach using SC3 as done here.

In principle, EMP analyses could be made in the region of the SCJ profiles reported above where the SCJ olivine Al concentration appears homogeneous. However, the $5x10^{14}/cm^2$ implant is worth >26% of the EMP signal from the olivine Al, so the implant would have to be sputtered away from local regions on SCJ adjacent to where the SIMS analyses were made. To remove the implant, the amount of sputtering would have to be much larger (about 0.3 micron) than the < 0.1 micron removed to sputter clean SC3. In addition to destroying significant amounts of the implant, the issue of redeposited sputtered implant Al would have to be evaluated. The above procedure has not been used in this study.

References

Ziegler J.F., Biersack J.P. and Ziegler M.D. (2008) SRIM: The stopping and range of ions in matter. SRIM Co. (Chester, Pa, USA), 398pp.